AD-A054 854 DOW CHEMICAL CO MIDLAND MICH THERMAL RESEARCH LAB F/G 20/13
CALCULATION OF THERMODYNAMIC PROPERTIES OF IDEAL GASES AT HIGH --ETC(U)
MAR 78 J R DOWNEY F44620-75-C-0048

UNCLASSIFIED AFOSR-TR-78-0960 NL

| OF |
AD
A054854

END
DATE
FILMED
7-78
DDC

AFOSR-TR- 78-0960

FOR FURTHER TRAN

AD A054854

AU NO.
DDC FILE COPY

CALCULATION OF THERMODYNAMIC PROPERTIES OF IDEAL GASES AT HIGH TEMPERATURES: MONATOMIC GASES

by

J. R. Downey, Jr.
Thermal Research
The Dow Chemical Company
Midland, Michigan

Supported by

U. S. Air Force Office of Scientific Research

Directorate of Aerospace Sciences

Joseph F. Masi - Staff Scientist

Contract No. F44620-75-C-0048

DDC
RECEIVED
JUN 8 1978
B

March 9, 1978

Approved for public release; distribution unlimited.

Qualified requestors may obtain additional copies from the Defense Documentation Center, all others should apply to the National Technical Information Service.

Conditions of Reproduction

Reproduction, translation, publication, use and disposal in whole or in part by or for the United Sates Government is permitted.

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
NOTICE OF TRANSMITTAL TO DDC
This technical report has been reviewed and is approved for public release IAW AFR 190-12 (7b).
Distribution is unlimited.
A. D. BLOSE
Technical Information Officer [redacted]

CALCULATION OF THERMODYNAMIC PROPERTIES OF IDEAL GASES AT HIGH TEMPERATURES: MONATOMIC GASES.

by

J. R. Downey, Jr.
Thermal Research Lab
The Dow Chemical Company
Midland, Michigan

Interim rept.,

Supported by

U. S. Air Force Office of Scientific Research
Directorate of Aerospace Sciences
Joseph F. Masi - Staff Scientist
Contract No. F44620-75-C-0048

AFOSR
TR-78-0960

34p.
9 March 1978
2308
B1

Approved for public release; distribution unlimited.

401089 LB

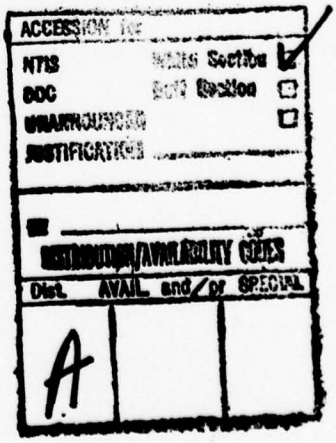
Qualified requestors may obtain additional copies from the Defense Documentation Center, all others should apply to the National Technical Information Service.

Conditions of Reproduction

Reproduction, translation, publication, use and disposal in whole or in part by or for the United Sates Government is permitted.

TABLE OF CONTENTS

		Page
	Abstract.	1
I.	Nature of the Problem	2
II.	The Translational Partition Function.	2
III.	The Electronic Partition Function	3
	A. The Problem	3
	B. Cut-off and Fill Procedures	6
	C. Effect of Cut-off and Fill Procedures on Thermodynamic Properties.	9
IV.	Plasmas	12
V.	Summary and Recommendations	13
	Bibliography.	16
	Appendix I	22



Abstract

The dual purpose of this report is to address the problems involved in extending the JANAF Thermochemical Tables for monatomic gases to higher temperatures (e.g. $T > 6000$ K), and the formulation of more definitive procedures for producing the tables in their present format. ($T \leq 6000$ K). Since there is a total lack of experimental thermochemical data for high temperature gases, statistical mechanics must be used to calculate the thermodynamic properties. Thus some discussion of statistical mechanics is necessary and this is included in a non-rigorous manner. The problem of finding a suitable cutoff procedure for the electronic partition function constitutes the body of this report. In the final section a recommended method of extending the calculations to higher temperature is advanced, and a brief discussion of the remaining problems in implementing this method is given. An annotated bibliography of relevant literature is included. A method of predicting the theoretical statistical weight for the electronic energy levels of the first 86 elements is presented in an appendix.

I. NATURE OF THE PROBLEM

For an ideal gas statistical mechanics may be used, in principle, to calculate the thermodynamic properties of any atom or molecule, no matter what the complexity. The partition function is separable into the various terms Q_{tr} (translational) and Q_i (internal).

$$Q = Q_{tr} \cdot Q_i \qquad [1]$$

Q_i may be written as a product of several terms; electronic, vibrational, rotational, etc. For a monatomic gas only the electronic term (Q_e) need be considered so

$$Q_{monatomic} = Q_{tr} \cdot Q_e \qquad [2]$$

If the terms Q_{tr} and Q_e can be accurately determined at all temperatures then the thermodynamic properties may be accurately calculated from Q via standard formulas (14, 15).

II. THE TRANSLATIONAL PARTITION FUNCTION

Q_{tr} is usually derived from a particle in a box procedure (14, 15), the only assumptions being the replacement of a summation of closely spaced levels by an integration and the applicability of Boltzmann (classical) statistics. The use of the integration presents no known problems since the translational energy levels are extremely close together. For translational motion Boltzmann statistics remains valid as long as

$$\frac{e^{\frac{\varepsilon}{kT}} (2\pi mkT)^{3/2} V}{N} >> 1 \qquad [3]$$

This condition is violated only under the condition that the density, proportional to N/V, becomes very high (14). This situation occurs in the interior of stars and also for the electron gas in metals, compounded

in the latter situation by m being lower by a factor of 2×10^3 than for any atomic or molecular case. Under these conditions quantum rather than classical statistics will be obeyed.

Under all other conditions classical statistics will be obeyed and Q_{tr} may be accurately calculated.† The high density conditions are immaterial for our purposes since most thermochemical tables are calculated for standard conditions, 1 atm pressure.

III. THE ELECTRONIC PARTITION FUNCTION

A. The Problem

The electronic partition function is usually calculated from equation 4. In the JANAF Thermochemical Tables (25) we have normally used observed values for the energy

$$Q_e = \sum_n g_n \exp\left(\frac{-\varepsilon_n}{kT}\right) \qquad [4]$$

levels, ε_n (16). There are several practical problems in this procedure. First, our prime source (16) is at least 20 years out of date. Thus, to do a thorough job, some means of obtaining an update of this information must be found. In the past the U. S. National Bureau of

† At temperatures near absolute zero the classical calculation of Q_{tr} will also break down. In addition to the non-applicability of Boltzmann statistics at these temperatures (see eq. 3), the thermal energy is such that only a small number of translational levels are accessible and the integration is no longer a valid approximation. We shall not be concerned with these deviations from classical behavior since they occur below 10K for atomic and molecular systems under standard conditions (1 atm pressure). For the electron gas these "low-temperature" deviations extend to ~1200K at one atmosphere pressure due to the low mass of the electron.

Standards (NBS) Atomic Energy Level Data Center has been of assistance on an informal basis and they have published updates (27, 28) for selected atoms and ions. However, even with the assistance of NBS we face increased time and money costs in the form of literature searching and retrieval and critical evaluation to arrive at the "best" atomic energy levels. This becomes more important at higher temperatures since the higher levels contribute more to the partition function (see equation 4) and it is generally in the high energy region that new levels are being discovered. As an example the NBS publication (16) lists approximately 120 energy levels for Ar^+ while a not-so-recent publication (17) lists approximately 200 new levels. If this situation is widespread it could lead to significant high temperature differences in the thermodynamic properties for many atomic species. However, even if all the atomic levels can be obtained for an atom (this is impossible, see below) severe difficulties occur in the computation of Q_e.

To understand the difficulty in computing Q_e one must first understand the basis of atomic structure. For a hydrogenlike atom, quantum mechanics leads to an exact solution for the energies of these levels as given in the familiar equation 5. Thus there are an

$$\varepsilon_n = R\left(1 - \frac{1}{n^2}\right),\ n = 1, 2, 3 \ldots .\infty \qquad [5]$$

infinite number of levels leading up to the ionization potential, IP(IP=R). The rapid initial increase of ε_n with principal quantum number, n, usually leads to the statement (14, 15) that all levels other than the ground state may be neglected for hydrogen-like atoms since the exponential term in equation 4 becomes vanishingly small. While it is true that this term becomes extremely small it remains finite and rapidly approaches its value for the ionization potential. Thus if one sums an infinite number

of such terms the partition function Q_e (and Q) becomes infinite. This is compounded by the fact that $g_n \propto n^2$ so the approach to infinity is more rapid. Although the details of atomic structure are different (and not exactly solvable) for non-hydrogen-like atoms it is still true that there are an infinite number of bound states so the same end result, $Q_e = \infty$, is obtained. The same is true for molecules.

Since this leads to infinite values of the thermodynamic functions for all substances at all temperatures this is clearly contrary to experience, as is the conclusion that the probability of finding a hydrogen atom in the ground state is zero, which is the logical extension of this theory (5). One concludes, therefore, that either quantum mechanics or statistical mechanics is in error. Strickler (5) has shown that the way out of this paradox is to realize that for large values of n the wave functions will not be hydrogenic, but will be described by the container due to the large volume of a single atom. Since this is essentially a particle in a box problem, there will then be a finite number of energy levels just as for Q_{tr}, resulting in a finite Q_e. He further shows that even if one assumes the flask to be the size of the known universe, Q_e will not differ significantly from unity for atomic hydrogen at 298.15 K, i.e., the ground state contribution only. A quick calculation shown that the excited states can no longer be ignored as the temperature increases; at 25,000 K for hydrogen each excited level contributes $\sim$.002 to Q_e, and this contribution will increase with temperature.

Since the ionization potential of hydrogen is higher than for most other atoms [only the rare gases are higher (16)] the situation will be more severe for other atoms. The worst cases will be those atoms with

the lowest ionization potentials, the alkali metals, followed by the alkaline earths and transition elements. For sodium the problem becomes serious at ∿5000 K (7). For the transition elements and rare earths there is the additional problem of a number of quite low lying levels which will make significant contributions even below room temperature.

What is needed is a generally applicable method of determining Q_e which will be valid at all temperatures. Since there are a finite number of energy levels, a reasonable approach would be to simply cut-off the summation process for Q_e at some point. In the next section we shall investigate various cut-off procedures that have been suggested.

B. Cut-off and Fill Procedures

Several cut-off procedures have been used in the past and they generally fall into these catagories:

- no dependence on temperature and pressure (10, 24)
- dependence on temperature only (1, 7, 9)
- dependence on temperature and pressure (density)(8, 11, 18, 20, 21)
- dependence on density of charged particles (3, 13, 22, 23)

The first category includes using the ground electronic level only or summing over some fixed number of levels which is usually arbritary (1) (to n = 5 for example, (24)). These methods generally fail at high temperatures for obvious reasons. The present JANAF method of summing over all observed levels falls in this category (no P or T dependence) and certainly has some validity in that the levels have been observed and therefore exist. However it is not known whether they exist in the gas under the standard condition (1 atm) to which the tables are applicable

and there remains the problem mentioned earlier of keeping up to date on all observed energy levels, see section III.A.

Methods in the second category generally use a quantity called the "ionization potential lowering" which is a function of temperature only. The theoretical basis of this method is that the effective ionization potential will be lowered due to collisions with surrounding atoms such that an outer electron with a binding energy less than kT will generally be released (ionization) in a collision (1). McChesney gives a simple derivation (3). Thus the summation in equation 4 is halted at ε_n = IP - kT. This cut-off technique has been used by several investigators (3, 16). McChesney (3) reports another ionization potential lowering method which is proportional to the square root of mkT (m = atomic mass) and has apparently not been used in any calculations. According to the derivation (3), these methods are strictly applicable only to plasmas where one has free electrons present. In addition it should be noted that at high enough temperatures all levels other than the ground state will be eliminated from the sum in equation 4. The method where the summation is halted at IP-kT will be referred to later as the TEMPER method as in the NASA program (1). McBride and Gordon (1) recommend this method and have used it in calculations (7).

The methods dependent on both P and T are mainly due to the assumption that each atom may occupy only a limited volume in space. These methods are often referred to as excluded volume methods and are, essentially, particle in a box methods. Fermi (11) and Bethe (18) both derived cut-off formulas based on these assumptions. Gurvich (8) and McChesney (3) give the derivation due to Bethe which assumes hydrogenic orbits and the molecular volume limited to the molar volume divided by Avogadro's number.

Bethe's criterion (at 1 atm pressure) then reduces to:

$$n_{max} = 2.461\ T^{1/6} \qquad (T = K) \qquad [6]$$

Fermi's criterion has a more complex formulation (8, 11) but as discussed by Gurvich (8) gives nearly the same values for n_{max}. The Bethe formulation, equation 6, is easy to implement though care must be taken to prevent discontinuities since n_{max} is allowed to change in integer increments only (8). This method of limiting the sum in equation 4 will be referred to later as the BETHE method.

The last general method of limiting the summation in equation 4 uses methods involving ionization potential lowering, the amount of which is a function of electron and ionized particle densities. These methods have been reviewed by McChesney (3) and are not further considered here since they apply to a plasma only and cannot be used for a single species as required in the JANAF tables; however, see section IV.

In addition to the cut-off method some decision must be made whether to include predicted, but unobserved, energy levels which lie below the cut-off point. If they are to be included some method of filling in the missing levels must be found. These levels can be predicted by the Rydberg or Rydberg-Ritz formulas (19) but this method is not compatible to computer application. McBride and Gordon (1) developed a method of predicting the total g_n for each principal quantum number n, for the first 20 elements. Several authors (1, 8) have shown that only a rough approximation of the energies of upper levels is needed so a simple method of calculating how many levels are missing can be combined with a rough approximation of their energy. The missing levels for any value of n are then predicted to lie at the energy of the highest known level for that value of n. This approximation becomes more accurate as n increases, since the atoms behave in a more hydrogenic manner. This

method will be referred to as the FILL procedure as in the NASA program (1). The FILL procedure has been extended to cover the entire periodic table excluding the lanthanides and actinides in Appendix 1.

C. Effect of Cut-Off and FILL Procedures on Thermodynamic Properties

The dependence of the various thermodynamic functions on the partition function Q is given as follows:

$$\frac{G^\circ_T - H^\circ_o}{RT} = \ln Q$$

$$\frac{C^\circ_p}{R} = \frac{T^2}{Q}\frac{d^2Q}{dT^2} - \frac{T}{Q}\frac{dQ^2}{dT} + \frac{2T}{Q}\frac{dQ}{dT}$$

$$\frac{H^\circ_T - H^\circ_o}{RT} = \frac{T}{Q}\frac{dQ}{dT}$$

$$\frac{S^\circ}{R} = \frac{T}{Q}\frac{dQ}{dT} + \ln Q$$

The dependence of each property on Q, and therefore on the cut-off and fill methods involved in Q_e, is different and must be evaluated separately. One expects C°_p/R to show the most radical behavior since it involves both first and second derivatives of Q. In order to investigate the effect of the various cut-off procedures we shall calculate the various thermodynamic properties of Na(g). As mentioned earlier the alkali metals have very low ionization potentials so this represents a worst-case approach.

The electronic energy levels and degeneracies for Na(g) were taken from Moore (16). The observed levels have a total degeneracy of 648 and extend to n = 59 although a large number of levels remain unobserved for the higher values of n. See Table 1 for a summary of these levels. The labels on the plots correspond to those in the NASA program (1), with the exception of BETHE, and are as follows:

ALLN - using all observed levels (16). This is the present JANAF method.

ALLN-FILL - using all observed levels and filling in missing levels using FILL option

TEMPER - summation over observed levels is cut-off at IP-kT

BETHE-FILL - summation over levels using cut-off from equation 6 and the FILL option

circles - using ground state only

dashed line - translational contribution only

Consult the previous section for further details on these method.

The effects of the various cut-off procedures on the thermodynamic properties of sodium are shown in Figures 1 and 2. A quick reference to these figures confirms that the largest effect is for the heat capacity where differences exceeding 1000 percent are noted near 5000 K. The least sensitive property is the free energy function, $-(G^\circ - H^\circ_0)/RT$, and this is fortunate since this term is important in equilibrium calculations. The largest deviations in the thermal properties arise when using the ALLN-FILL procedure and this will become more severe as energy levels are discovered to higher n values. For these reasons this procedure has not been used in the past and will not be considered for future use since it obviously overestimates the contribution of upper states. As shown in Table 2 the total degeneracy using this procedure is 140,410 and will increase rapidly ($\sim$ as n^2) as n increases.

As shown in Figures 1 and 2 the TEMPER method yields the least deviation from the classical (ground state only) case. This is because more levels are eliminated from the summation in equation 4 as the temperature increases. In fact at high enough temperatures, see Table

2, all levels are cut-off except the ground state. The FILL option has virtually no effect when using the TEMPER method since the levels are rapidly cut-off to a point where most levels have been observed. For sodium the TEMPER-FILL results are imperceptibly higher than the TEMPER results. The main objection to the TEMPER method is a philosophical one since this method leads to a narrower distribution of electrons over a set of energy levels with increasing temperature which is the opposite of what is expected from fundamental principles (Boltzmann distribution).

The BETHE-FILL method results in thermodynamic properties slightly higher than for the ALLN method for sodium as illustrated in Figures 1 and 2. Although not illustrated, the BETHE method (without the FILL option) lies approximately midway between the curves for the ALLN and TEMPER methods. Of these methods the BETHE-FILL method seems preferable since it avoids the problem of unobserved levels inherent in the others. This procedure has been used by Gurvich (8) although his procedure for predicting the energies and numbers of unobserved levels is slightly different than the FILL procedure used here.

If Na(g) represents a worst-case approach then He(g) represents a best-case approach since it has the highest ionization potential of any neutral atom (16). Its thermodynamic properties are illustrated in Figures 3 and 4 and the same general behavior of the various procedures is observed. The big difference is the temperature at which the various cut-off procedures have an effect. Neglecting the ALLN-FILL method, Na(g) shows deviations beginning at ∿4000 K while He(g) does not show deviations until ∿20000 K.

IV. PLASMAS

Although we are interested primarily in the calculation of properties of individual species it seems of interest to mention some of the salient properties of plasmas, i.e. mixtures of atoms, ions, and electrons in thermal equilibrium. The reason for this is that at temperatures high enough for significant contributions from excited states in Q_e to be important, one begins to get significant amounts of ionization, e.g. $Na(g) \rightarrow Na^+(g) + e^-(g)$. Presumably the primary use of JANAF tables at such temperatures would be to calculate equilibrium properties of these systems. Several authors (3, 6, 9, 10, 12, 13, 20, 21, 22) have discussed the details of plasma and shock wave calculations which are usually done in an iterative procedure; we shall only consider two items of importance to our discussion of individual species. The effect of a charged species (ion or electron) on a neutral atom is twofold; modification of the energies of the electronic levels (Stark effect) and lowering of the ionization potential, both due to the long range Coulomb effect. Both of these will be a function of distance and ion density.

The Stark effect is usually ignored since its greatest effect will be on upper electronic levels and there are no simple methods for exact calculations. Use of neutral atom levels in a plasma is therefore an approximation. Lowering of the ionization potential due to charged species leads to a family of cut-off procedures (3) which are dependent on temperature and/or charge density. McChesney (3) argues against the use of the BETHE method in plasmas while other authors have used this method (20, 21). Capitelli et al. (6) and Woolley (23) have shown that the equilibrium properties of these plasmas are virtually independent of

the cut-off procedure used. Capitelli et al. (6) have shown that this is due to a compensation between reactional and frozen terms which are dependent on electronic excitation (Q_e). Therefore although the cut-off and FILL procedures have a large effect on the thermodynamic properties of individual species there is only a small effect on equilibrium properties in plasmas. However the methods should not be mixed as this may lead to gross inconsistencies.

In dealing with real systems such as plasmas one is always faced with assigning a portion of the interaction to standard states and another portion to an equation of state. This is not unlike treating dissociation in molecular systems where one may treat the system as a perfect solution of three components or as a non-ideal solution of one or two components with any other contributions accounted for by the equation of state (30). In either the atomic or molecular cases the choice and division of components is arbitrary to some extent, but the important thing is that consistency is maintained so that all of the energy levels are counted once and once only. The choice of cutoff procedure allots the electronic energy levels to those belonging to the associated species (e.g., Na) and the dissociated (ionized) species (e.g., $Na^+ + e^-$). In order to maintain consistency the same cutoff procedure must be used for all species or a large bias in the equilibrium properties of plasmas may result.

V. SUMMARY AND RECOMMENDATIONS

It has been shown that calculated high temperature thermodynamic properties are greatly influenced by the method used to cut-off (and supply missing levels to) the electronic partition function. Despite this effect on the properties of individual species, the cut-off and

FILL procedures appear to have little effect on the equilibrium properties of a mixture as long as the same method is used for all species. This is fortuitous and makes the choice of a cut-off procedure somewhat less critical. Nevertheless a procedure is necessary that is easy to implement and as accurate as possible. It is believed that the BETHE cut-off procedure combined with the FILL option provides the most reasonable alternative at our present state of knowledge. This method will be used on future JANAF Tables. This method requires minimum knowledge of the observed spectrum (to n = 13 at 20,000 K) and fills in missing levels so it should be reasonably independent of new observations. This minimizes the literature search aspects.

Based on the limited calculations already performed it appears likely that switching from the ALLN to the BETHE-FILL procedure will cause only minor differences below 6000 K for most current JANAF Tables. The largest changes are expected to be for the alkali metals. If the Tables are extended to higher temperatures the BETHE-FILL procedure should yield more uniform results. The upper limit to validity of this procedure (or any of the other cut-off procedures) is not known but it seems likely that it will be satisfactory to at least 10,000 K for most species.

There is no absolute means of determining which method is correct based on measured data since appropriate experiments at these high temperatures do not seem feasible in the near future. Therefore, it seems desirable to incorporate some statement concerning at what temperature the cut-off criteria becomes important and some measure of the uncertainty due to it. The free energy function or the entropy appears suitable since the values calculated via any cut-off procedure show a

continuous increase with temperature. Of these two, the free energy function $[-(G^\circ - H_{298})/T]$ seems to be preferable since it relates the free energy of formation at any temperature to the heat of formation at 298.15 K and, therefore, enters directly into equilibrium calculations. It is recommended that the temperature at which the difference in the free energy function, calculated via the BETHE-FILL and TEMPER procedures, reaches 0.1 gibbs/mol should be tabulated on future JANAF tables as a measure of uncertainty due to the cut-off procedures. For Na(g) this is ∿5100 K and for He(g) it is ∿24,400 K. These represent essentially the worst and best cases, respectively, for neutral atoms. The ionization potentials for positively charged ions are generally quite high and their properties will be valid to even higher temperatures before uncertainties due to cut-off methods arise.

Implementation of the BETHE-FILL procedure for general usage will require several tasks. First, the BETHE procedure must be incorporated into a computer program in a manner which will avoid discontinuities in the thermal functions. Calculations for this report were done, in part, by hand to avoid discontinuities. Gurvich (8) has described a method which is applicable to computer usage so no problems should arise in this area. The FILL procedure is already implemented in one of our computer programs (1) for the first 20 elements and will be extended to the remaining elements using the results of Appendix I.

Bibliography

1. B. J. McBride and S. Gordon, NASA TN D-4097, 1967. Discussion of cut-off methods and fill methods for first 20 elements; program to calculate same.

2. M. Klein, in "Physical Chemistry", Vol. 1, H. Eyring, D. Henderson, and W. Jost, eds, Academic, New York, 1971. General discussion of divergence and cut-off methods.

3. M. McChesney, Can J. Phys., 42, 2473 (1964). Excellent discussion of the cut-off procedures in plasmas.

4. K. L. Shipley, J. Appl. Phys., 40, 3037 (1969). Shows effect of excited electronic levels on Q for C_2.

5. S. J. Strickler, J. Chem. Ed., 43, 364 (1966). A rather naive discussion of the divergence problem with no solutions proposed.

6. M. Capitelli, E. Fiococelli, and E. Molinari, Z. Naturforsch., 26a, 672 (1971). Divergence problems in a plasma are discussed and found to be insignificant as opposed to those for a single species.

7. B. J. McBride, S. Heimel, J. G. Ehlers, and S. Gordon, NASA SP-3001, 1963. Discussion of cut-off methods - used kT method.

8. L. V. Gurvich et. al., AD 659 660, 1967, p. 129 ff. Discussion of excluded volume methods due to Fermi and Gurvich (Bethe).

9. H. Myers, J. H. Buss, and S. W. Benson, Planetary and Space Science, 3, 257 (1961), see p. 261. Used kT limit for plasmas.

10. H. Margenau and M. Lewis, Rev. Mod. Physics, 31, 569 (1959), see pp 594 ff and p. 604. Discusses merging and drowning of levels in plasmas and cut-off criteria (n = 6 to n = 7).

11. E. Fermi, Z. Phys., 26, 54 (1924). Volume exclusion method.

12. L. Haar, in "Kinetics, Equilibria and Performance of High Temperature Systems," Proc. 1st Conf. Western States Sect. Combustion Inst., G. Bahn and E. Zukoski, eds, Butterworths, Washington, 1960. Cluster theory in plasmas.

13. H. Krempl, in "Physical Chemistry", Vol. I, H. Eyring, D. Henderson, and W. Jost, eds., Academic, New York, 1971, pp 551 ff. Truncation methods based on various radii.

14. W. J. Moore, "Physical Chemistry", 3rd ed., Prentice-Hall, Englewood Cliffs, N.J., 1964, Chapter 15.

15. J. E. Mayer and M. G. Mayer, "Statistical Mechanics", Wiley, London, 1940.

16. C. E. Moore, NBS Circular 467, Vols. I, II, III, 1949, 1952, 1958. Atomic energy level tabulation.

17. L. Minnhagen, Arkiv. Physik, 25, 203 (1963). Ar^+ energy levels.

18. H. Bethe, Office of Scientific Research and Development Report #369, 1942. BETHE cut-off criteria.

19. H. Kuhn, "Atomic Spectra", Academic Press, 1962.

20. H. N. Olsen, Phys. Fluids, 2, 614 (1959). Used modified BETHE method in plasmas.

21. J. W. Bond, Phys. Rev., 105, 1683 (1957). Used modified BETHE method in plasmas.

22. H. R. Griem, Phys. Rev., 128, 997 (1962). Cut-off at lowered IP in plasma.

23. H. W. Woolley, AFSWC-56-34, 1957. Cluster theory of plasmas and equilibrium properties to 4,000,000°K.

24. J. Hilsenrath, C. G. Messina, and W. H. Evans, AFWL-TDR-64-44 (AD-606 163), 1964. Calc. for 73 atoms (and 1st and 2nd ions) using n = 5 cut-off, tabulates effect of cut-off on free energy function to 10,000 K.

25. D. R. Stull and H. Prophet, "JANAF Thermochemical Tables," 2nd ed., NSRDS-NBS 37, June, 1971; M. W. Chase et. al., J. Phys. Chem. Ref. Data, 3, 311 (1974); M. W. Chase et al., J. Phys. Chem. Ref. Data, 4, 1 (1975).

26. G. Herzberg, "Atomic Spectra and Atomic Structure," 2nd ed., Dover Pub., New York, 1944.

27. J. Reader and J. Sugar, J. Phys. Chem. Ref. Data, 4, 353 (1975).

28. J. Sugar and C. Corliss, J. Phys. Chem. Ref. Data, 6, 317 (1977).

29. H. M. Rosenstock, K. Draxl, B. W. Steiner and J. T. Herron, J. Phys. Chem. Ref. Data, 6, (1977), Supplement 1.

30. G. N. Lewis, M. Randall, K. S. Pitzer and L. Brewer, "Thermodynamics," Second Edition, McGraw-Hill, New York, 1961, pp. 273-77, 307-8.

TABLE 1

A Summary of Some of the Electronic Energy Levels of Na(g)

n	ε range, cm^{-1}	g_n	
		observed	predicted*
3	0-29173	18	18
4	25740-34589	32	32
5	33201-37060	50	50
10	39983-40351	32	200
15	40901-40958	16	450
20	41150	6	800
30	41320	6	1800
40	41378	6	3200
50	41404	6	5000
59	41417	6	6962
IP†	41450		

* using FILL option

† ionization potential

TABLE 2

Highest Principal Quantum Number and Total Number of Levels Used in Determination of Q_e for Na(g)

	6000 K		10000 K		40000 K	
	n	Σg_i	n	Σg_i	n	Σg_i
ALLN	59	648	59	648	59	648
ALLN-FILL	59	140,410	59	140,410	59	140,410
TEMPER	6	102	5	28	3	2†
BETHE-FILL	10	881	11	1120	14	2200
BETHE	10	298	11	322	14	374

† ground state only

FIGURE 1. HEAT CAPACITY AND ENTROPY FOR SODIUM GAS

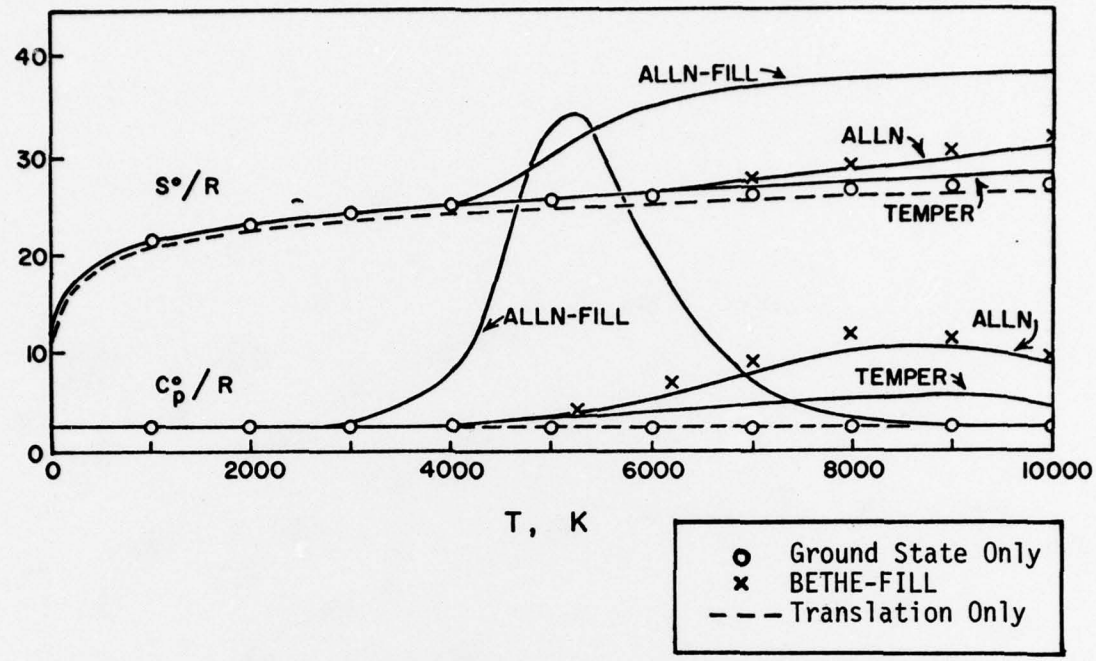


FIGURE 2. FREE ENERGY FUNCTION AND ENTHALPY FOR SODIUM GAS

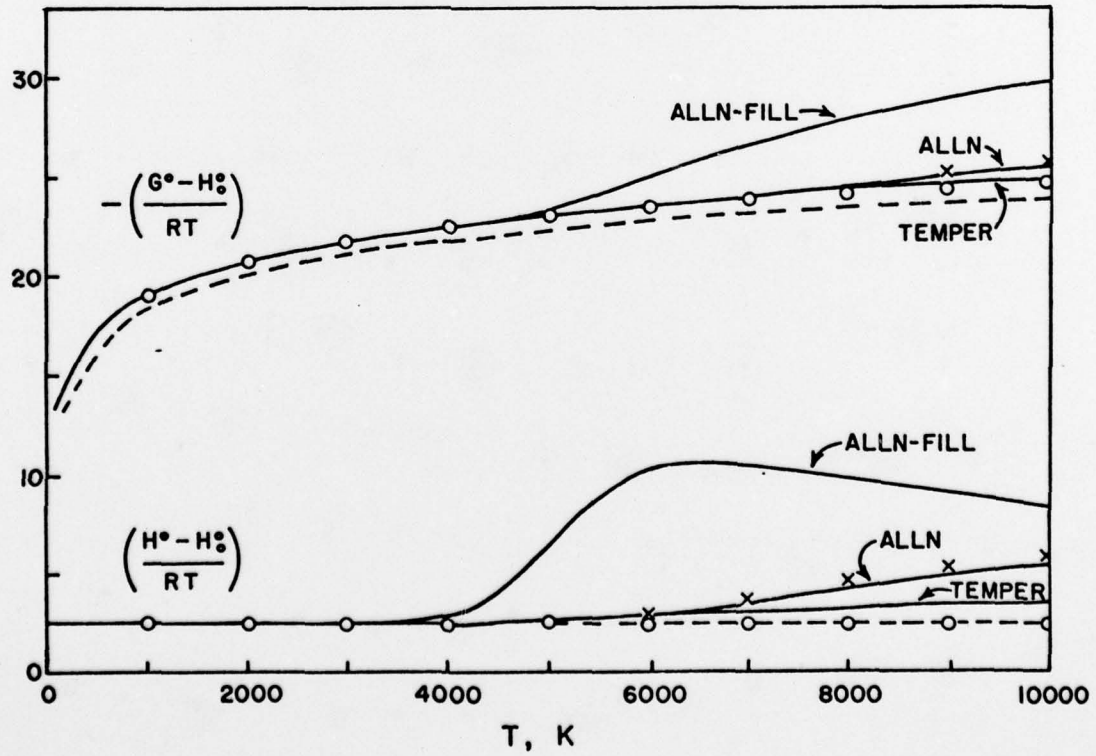


FIGURE 3. HEAT CAPACITY OF HELIUM GAS

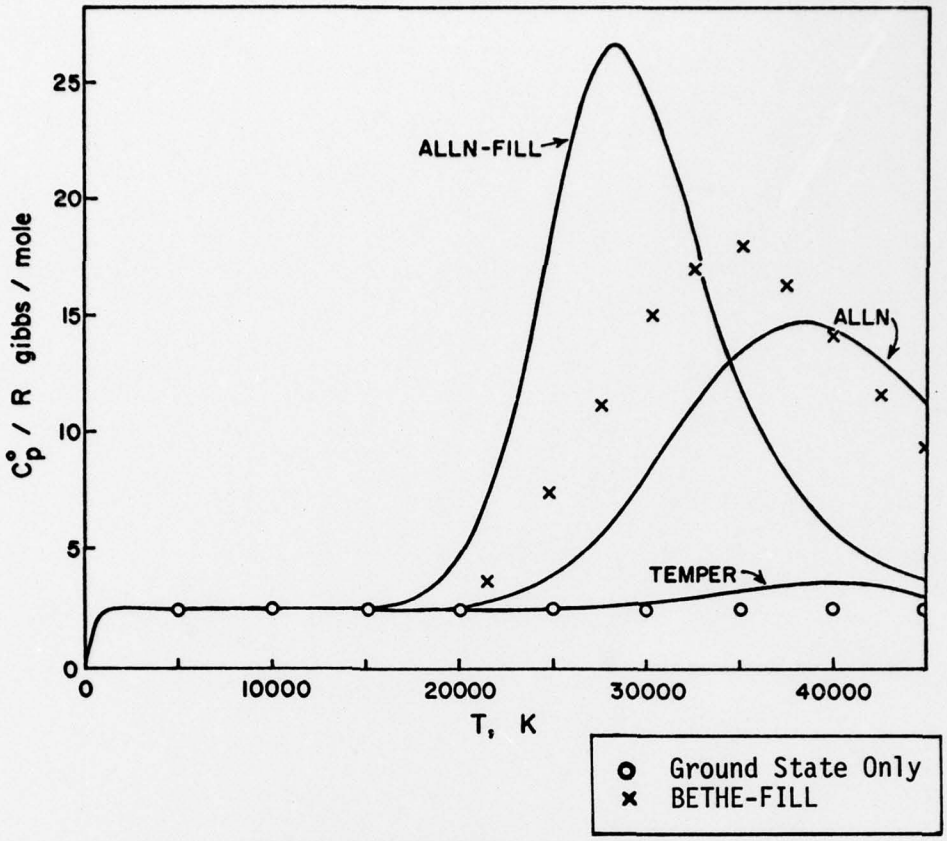
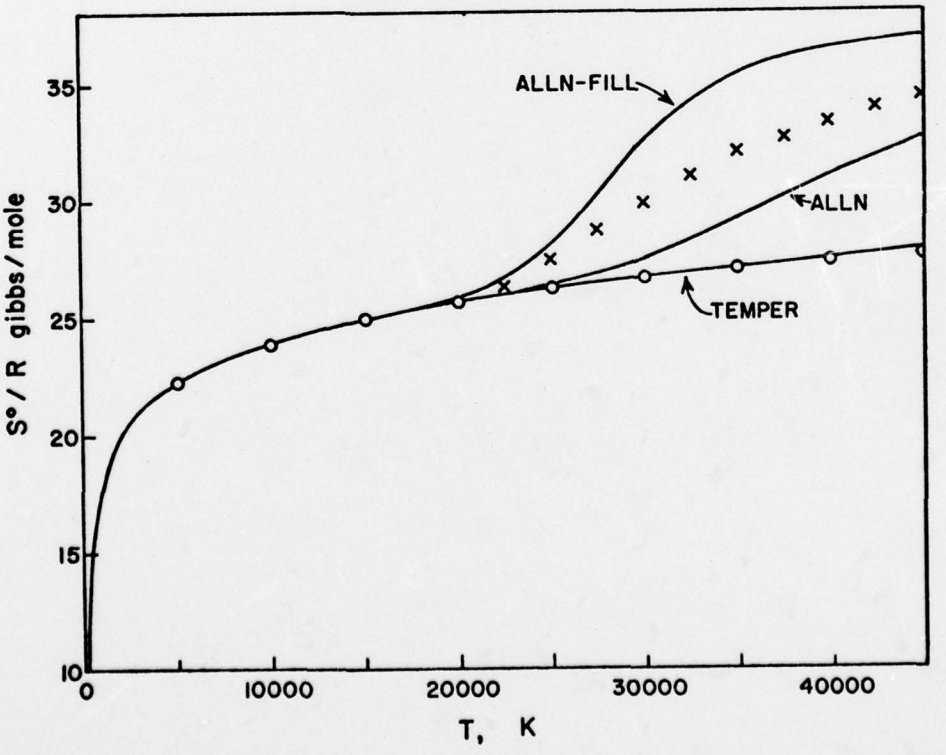


FIGURE 4. ENTROPY OF HELIUM GAS



Appendix I. Prediction of Total Quantum Weights From Electronic Configurations

In order to apply the FILL option (1) one must be able to predict the total quantum weight (degeneracy) arising from various electronic configurations. This may be done by referring to the predicted terms as derived from atomic theory (see Tables 10 and 11 of ref. 26). The quantum weights arising from these terms may then be calculated in the usual manner from atomic theory (26). The results for some simple cases are given in Table 3 for non-equivalent electrons (different n, ℓ subgroups) and in Table 4 for equivalent electrons (having the same n and the same ℓ). The results of Table 3 may be verified by remembering that there are 2 ways to place one electron in an s orbital (s = +1/2 or s = -1/2), 6 ways to place one electron in the 3 p orbitals, etc. The Pauli principle restricts the placement of multiple electrons having the same values of n and ℓ and leads to the differences between Tables 3 and 4.

We now wish to calculate the total quantum weight allowed for any atom assuming excitation of only the most easily excitable electron. The calculation is outlined here for the magnesium atom whose ground state configuration is $[Ne]3s^2$. Atomic theory tells us that the allowable configurations within the n=3 shell are $[Ne]3s^2$, [Ne]3s3p, and [Ne]3s3d. Reference to Tables 3 and 4 shows that the total quantum weight of these configurations is 33. Assuming excitation of one electron to the n=4 shell gives allowable configurations of [Ne]3s4s, [Ne]3s4p, [Ne]3s4d, and [Ne]3s4f which we write in shorthand notation as [Ne]3s4spdf indicating one electron in the 3s orbital and one electron somewhere in the n=4 shell. Reference to Table 3 gives a

total quantum weight (G) of 64 for these configurations while for the n=5 shell we get G=100 for [Ne]3s5spdfg. The values of G for these last two examples may be given by $G=bn^2$ where n is the principal quantum number of the outer shell and b for the current example is 4. The procedure may be extended to all higher values of n. This is the FILL method originated by McBride and Gordon (1). This same procedure will work, without exception, for the first 18 elements and our results (Table 5) agree with those of McBride and Gordon (1).

Beginning with potassium (at. no.=19) this procedure should be modified because the orbitals no longer fill in sequence by n value. Instead the [Ar]3d and [Ar]4s terms are of approximately equal energy; for potassium the ground state is [Ar]4s and there are low lying states from the [Ar]3d configuration. We choose to count these states from "inner" configurations as part of the ground state (n=4) quantum weight. For potassium we arrive at a total quantum weight of 42 for the configurations [Ar]4spdf and [Ar]3d using Table 3 and 4. This is higher than that derived by McBride and Gordon (1) since they did not count the [Ar]3d levels. The excited state quantum weights for potassium can be calculated using b=2 as derived using configurations such as [Ar]5spdfg, [Ar]6spdfgh, etc.

Using the procedure outlined above for potassium allows one to extend the treatment to the transition elements and throughout the remainder of the periodic Table. However, in the transition series it seems advisable to impose limitations based on the non-observance of terms arising from certain electronic configurations. This is an empirical procedure and must be recognized as such but it is designed to prevent counting of terms which, most likely, occur above the ionization

limit. The general ground state configuration in the first transition series is $[Ar]4s^2 3d^m$. Other possible (inner) configurations involving n=4 terms are $[Ar]4s3d^{m+1}$, $[Ar]4s3d^m 4pdf$, $[Ar]3d^{m+1}4pdf$, $[Ar]3d^{m+2}$, and $[Ar]4s^2 3d^{m-1}4pdf$. Of these, terms arising from the last configuration are not observed in the first transition series except for Cr and Fe where $[Ar]4s^2 3d^{m-1}4p$ terms are seen very near the ionization limit [16,27,28]. Therefore it seems likely that most of the terms involving the $[Ar]4s^2 3d^{m-1}4pdf$ configuration lie above the ionization limit so we do not count them. For similar reasons we do not count terms arising from $[Ar]4s3d^m 4f$ or $[Ar]3d^{m+1}4f$ configurations. Likewise, when excitation to orbitals of higher principal quantum numbers are considered we count only $[Ar]4s3d^m 5spd$ and $[Ar]3d^{m+1}5spd$ terms and their counterparts for higher orbitals. Because of this, a constant quantum weight is predicted for excitation to each of the upper levels rather than one which increases with n^2 as predicted earlier for the non-transition atoms. In Table 5 we list the value of this constant, c, for the transition elements. Beginning with Cu, the filled d^{10} shell begins to show its exceptional stability and we consider only excited states arising from this configuration and return to the previous mechanism for calculating G for the excited states.

The procedure outlined above may be extended throughout the rest of the periodic Table with only two additional modifications. The first of these is that beginning with silver, we count configurations involving a single 4f electron as part of the ground state degeneracy (Σg), e.g. $[Kr]4d^{10}4f$ for Ag and $[Kr]5s^2 5p^4 4f$ for I. These contributions are allowed through lanthanum, after which the 4f shell fills completely. We have not worked out the results for the lanthanide series (4f electrons being added) since there is no interest in these elements by the JANAF

group at the present time. The final modification is the counting of configurations involving single 5f or 5g electrons as part of the ground state Σg beginning with gold.

The results are summarized through atomic number 86 (Radon) in Table 5. These values refer to the neutral atom. Since the electronic structure of positive ions is similar to that of the isoelectronic neutral atom (16), the results in Table 5 may be applied to positive ions by taking care to use values of Σg and b (or c) corresponding to the isoelectronic neutral atom. Thus, for Mg^{++} one would use the values for Ne from Table 5. This same extension must not be made to negative ions. Because of the low ionization potential of most negative monatomic ions, they are usually treated as if there are no bound excited states (8,25). A recent critical evaluation by Rosenstock et. al. (29) lists only three negative monatomic ions containing observed bound excited states; C^-, Mg^- and Si^-. Only a single bound excited state was observed for each of these. Bound excited states have been theoretically predicted for other negative ions (H^-, Be^-, Al^-, and P^-) but have not been observed (29). Therefore we favor using only observed electronic states when calculating thermodynamic properties of negative monatomic ions.

TABLE 3. QUANTUM WEIGHTS OF NON-EQUIVALENT ELECTRONS

Electron Configuration	Total Quantum Weight Of Terms
ss	4
sp	12
sd	20
sf	28
sg	36
pp	36
pd	60
dd	100
sss	8
ssp	24
ssd	40
spp	72
spd	120
ppp	216
ppd	360

TABLE 4. QUANTUM WEIGHTS OF EQUIVALENT ELECTRONS

Electron Configuration	Total Quantum Weight Of Terms
s^1	2
s^2	1
$p^1(p^5)$	6
$p^2(p^4)$	15
p^3	20
$p^6(p^o)$	1
$d^1(d^9)$	10
$d^2(d^8)$	45
$d^3(d^7)$	120
$d^4(d^6)$	210
d^5	252
$3^{10}(d^o)$	1
$f^{14}(f^o)$	1

TABLE 5. PARAMETERS USED WITH THE FILL PROCEDURE

Atomic Number	Symbol	Σg	b(or c*)	Atomic Number	Symbol	Σg	b(or c*)
1	H	2	2	38	Sr	670	4
2	He	1	4	39	Y	1260	1170*
3	Li	8	2	40	Zr	3855	3780*
4	Be	13	4	41	Nb	7992	8100*
5	B	6	2	42	Mo	11676	12096*
6	C	15	12	43	Te	12216	12852*
7	N	20	30	44	Ru	9135	9720*
8	O	15	40	45	Rh	4780	5130*
9	F	6	30	46	Pd	1666	1800*
10	Ne	1	12	47	Ag	394	2
11	Na	18	2	48	Cd	125	4
12	Mg	33	4	49	In	92	2
13	Al	16	2	50	Sn	351	12
14	Si	75	12	51	Sb	860	30
15	P	170	30	52	Te	1135	40
16	S	215	40	53	I	846	30
17	Cl	156	30	54	Xe	337	12
18	Ar	61	12	55	Cs	124	2
19	K	42	2	56	Ba	1138	4
20	Ca	426	4	57	La	2200	1170*
21	Sc	1260	1170*	Lanthanide series-4f shell filled			
22	Ti	3855	3780*	72	Hf	3855	3780*
23	V	7992	8100*	73	Ta	7992	8100*
24	Cr	11676	12096*	74	W	11676	12096*
25	Mn	12216	12852*	75	Re	12216	12852*
26	Fe	9135	9720*	76	Os	9135	9720*
27	Co	4780	5130*	77	Ir	4780	5130*
28	Ni	1666	1800*	78	Pt	1666	1800*
29	Cu	362	2	79	Au	434	2
30	Zn	61	4	80	Hg	205	4
31	Ga	30	2	81	Tl	132	2
32	Ge	159	12	82	Pb	591	12
33	As	380	30	83	Bi	1460	30
34	Se	495	40	84	Po	1935	40
35	Br	366	30	85	At	1446	30
36	Kr	145	12	86	Rn	577	12
37	Rb	74	2				

*This is the c value which represents the total quantum weight for each value of n above the ground state principal quantum number.

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: AFOSR-TR- 78-0960	2. GOVT ACCESSION NO. / 3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): CALCULATION OF THERMODYNAMIC PROPERTIES OF IDEAL GASES AT HIGH TEMPERATURES: MONATOMIC GASES	5. TYPE OF REPORT & PERIOD COVERED: INTERIM
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): J R DOWNEY, JR	8. CONTRACT OR GRANT NUMBER(s): F44620-75-C-0048
9. PERFORMING ORGANIZATION NAME AND ADDRESS: DOW CHEMICAL COMPANY, THERMAL RESEARCH, MIDLAND, MI 48640	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 2308B1, 61102F
11. CONTROLLING OFFICE NAME AND ADDRESS: AIR FORCE OFFICE OF SCIENTIFIC RESEARCH/NA, BLDG 410, BOLLING AIR FORCE BASE, D C 20332	12. REPORT DATE: March 1978
	13. NUMBER OF PAGES: 31
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report): UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

ENTHALPY
ENTROPY
GIBBS ENERGY FUNCTION
HEAT CAPACITY
MONATOMIC GASES
PARTITION FUNCTIONS
THERMOCHEMICAL TABLES
≤ or =

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The dual purpose of this report is to address the problems involved in extending the JANAF Thermochemical Tables for monatomic gases to higher temperatures (e.g. T>6000 K), and the formulation of more definitive procedures for producing the tables in their present format (T≤6000 K). Since there is a total lack of experimental thermochemical data for high temperature gases, statistical mechanics must be used to calculate the thermodynamic properties. Thus some discussion of statistical mechanics is necessary and this is included in a non-rigorous manner. The problem of finding a suitable cutoff procedure for the electronic partition function constitutes the body of this

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

report. In the final section a recommended method of extending the calculations to higher temperature is advanced, and a brief discussion of the remaining problems in implementing this method is given. An annotated bibliography of relevant literature is included. A method of predicting the theoretical statistical weight for the electronic energy levels of the first 86 elements is presented in an appendix.